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HEAT-RESISTANT ALLOY HAVING EXCELLENT HIGH-TEMPERATURE CORROSION RESISTANCE

(Koon Taishokusei no Sugureta Tainetsu Gokin)

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SPECIFICATION

I. Title of the Invention

Heat-Resistant Alloy Having Excellent High-Temperature Corrosion Resistance

II. Claims

(1) A heat-resistant alloy having excellent high-temperature corrosion resistance, which is characterized by comprising

C 0.05 - 0.25%, Si 1.00% or less, Mn 5.0 - 15.0%, Ni 35.0 - 65.0%, Cr 20.0 - 35.0%, N 0.10 - 0.60%, balance Fe as well as impurity elements by weight ratio.

(2) A heat-resistant alloy having excellent high-temperature corrosion resistance, which is characterized by comprising

C 0.05 - 0.25%, Si 1.00% or less, Mn 5.0 - 15.0%, Ni 35.0 - 65.0%, Cr 20.0 - 35.0%, N 0.10 - 0.60%, and one, two or more of Mo 0.05 - 2.00%, W 0.05 - 2.00%, V 0.05 - 3.00%, Nb 0.05 - 3.00%, B 0.0005 - 0.0100%, balance Fe as well as impurity elements by weight ratio.

(3) A heat-resistant alloy having excellent high-temperature corrosion resistance, which is characterized by comprising

C 0.05 - 0.25%, Si 1.00% or less, Mn 5.0 - 15.0%, Ni 35.0 - 65.0%, Cr 20.0 - 35.0%, N 0.10 - 0.60%, and one, two or more of Al 0.01 - 0.50%, rear-earth elements 0.005 - 0.100%, Ca 0.0005 - 0.0200%, Mg 0.0005 - 0.0200%, balance Fe as well as impurity elements by weight ratio.

(4) A heat-resistant alloy having excellent high-temperature corrosion resistance, which is characterized by comprising

C 0.05 - 0.25%, Si 1.00% or less, Mn 5.0 - 15.0%, Ni 35.0 - 65.0%, Cr 20.0 - 35.0%, N 0.10 - 0.60%, one, two or more of Mo 0.05 - 2.00%, W 0.05 - 2.00%, V 0.05 - 3.00%, Nb 0.05 - 3.00%, B 0.0005 - 0.0100%, and one, two or more of Al 0.01 - 0.50%, rear-earth elements 0.005 - 0.100%, Ca 0.0005 - 0.0200%, Mg 0.0005 - 0.0200%, balance Fe as well as impurity elements by weight ratio.

III. Detailed Description of the Invention

This invention relates to a high-temperature heat-resistant alloy having excellent high-temperature corrosion resistance, high-temperature strength and producible with the dissolution of

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[1] Numbers in the margin indicate pagination in the foreign text.

air which can be used as a heat-resistant material of exhaust valve of a gasoline engine.

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The exhaust valve of a gasoline engine is exposed to a high-temperature corrosive exhaust gas and used under severe conditions such as high-speed running at a high temperature of 800°C or above. CO_2, H_2O and residual O_2, etc. exist in the high-temperature combustion gas, the valve is subjected to oxidation due to the compounds, particularly, the valve face is violently eroded by reaction products ($PbSO_4$, PbBrCl, $Pb_3(SO_4)_2$, etc. of lead oxide that is produced by burning tetraethyl lead or tetramethyl lead added into gasoline as antiknock agent and S, Cl, Br, P, etc. contained as impurities in gasoline.

Moreover, a large tensile stress and a bending stress act on the valve head during seating due to the tension of valve spring and inertia force of valve itself.

21-4N steel (Fe-21Cr-9Mn-4Ni-0.5C-0.4N) is given as a material most frequently used now for the valve of gasoline engine in Europe, USA and Japan.

However, even high output and high speed have been made in the latest high-performance engine, the high-temperature corrosion resistance and the high-temperature strength are insufficient in said 21-4N steel under such severe conditions,

and a condition of hard-to-resist to uses also appears, thus the development of alloys having much more excellent high-temperature corrosion resistance and high-temperature strength than 21-4N steel has been demanded.

Corresponding to such situation, Ni-based alloys or bush metal valve of stellite tend to be used in the exhaust valve recently. However, the Ni-based alloys increase the valve cost because the material is expensive, in addition, they have insufficient corrosion resistance against S-containing high-temperature combustion gas in a high-load engine.

Furthermore, the cost of bush metal valve of stellite is high because the metal bushing is complicated and considerable man power is needed as well as properties as exhaust valve are also insufficient in a high-load engine.

This invention was to eliminate such drawbacks of conventional steels, and the inventor repeated various studies, consequently he improved the corrosion resistance due to S-containing molten lead oxide (called composite lead oxide corrosion resistance hereafter) by substituting a part of Ni of said Ni-based alloy to contain Mn therein, and this invention is an alloy having an excellent high-temperature corrosion resistance and an equal high-temperature strength as compared with the Ni-based alloy which has been used before and is a much

cheaper high-temperature corrosion-resistant alloy by using Ti, Al, etc. having no effects of the corrosion resistance at high temperatures and N, C producible with the dissolution of air as reinforcing elements for increasing the strength at high temperatures.

The invented alloy is cheaper than the metal bushing valve of stellite and has excellent properties because it does not need complicated processes like stellite bushing in the valve manufacture and is similarly producible by upset forging as conventional 21-4N steel exhaust valve.

As described above, the invented alloy can be widely used in various heat-resistant parts, heat-resistant tool material, high-temperature sliding member, etc. as well as exhaust valve because it has excellent high-temperature corrosion resistance, high-temperature oxidation resistance and high-temperature strength.

The invented alloy will be explained in detail below.

The first invented alloy contains C 0.05 - 0.25%, Si 1.00% or less, Mn 5.0 - 15.0%, Ni 35.0 - 65.0%, Cr 20.0 - 35.0%, N 0.10 - 0.60%; the second invented alloy further contains one, two or more of Mo 0.05 - 2.00%, W 0.05 - 2.00%, V 0.05 - 3.00%, Nb 0.05 - 3.00% and B 0.0005 - 0.0100% in the first invented alloy and further raises the high-temperature strength without

much deteriorating the high-temperature corrosion resistance of said first invented alloy; the third invented alloy further contains one, two or more of Al 0.01 - 0.50%, rear-earth elements 0.005 - 0.100%, Ca 0.0005 - 0.0200% and Mg 0.0005 - 0.0200% in the first invented alloy to raise the thermal workability and high-temperature strength of the first invented alloy; and the fourth invented alloy further contains one, two or more of Al 0.01 - 0.50%, rear-earth elements 0.005 - 0.100%, Ca 0.0005 - 0.0200%, Mg 0.0005 - 0.0200% in the second invented alloy to raise the thermal workability and the high-temperature toughness of the second invented alloy (by weight ratio).

Reasons for limiting the composition of the invented alloy are explained below.

C solid dissolves in a part of ground mass to reinforce it and forms carbides to reinforce base material. The reinforcement of base material by carbides is effective, but the effect is small

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if C is less than 0.05% while the thermal workability is markedly impaired if C is more than 0.25%, therefore the range of C was taken as 0.05 - 0.25%.

Si solid dissolves in ground mass to reinforce it and improves the high-temperature oxidation resistance, but the

high-temperature lead oxide corrosion resistance is impaired if Si is more than 1.00%, therefore the upper limit of Si was taken as 1.00%.

Mn markedly improves the composite lead oxide corrosion resistance of high N alloy containing S compounds and other impurities. Fig. 1 shows the effect of Mn on the composite lead oxide corrosion resistance, and it is known from Fig. 1 that Mn markedly improves the corrosion resistance if Mn is 5.0% or more. Therefore, the lower limit of Mn was taken as 5.0%.

If Mn is more than 15%, a low-melting Ni-Mn eutectic crystal produces and the thermal workability becomes markedly difficult, therefore the upper limit of Mn was taken as 15.0%.

Ni is essential to obtain a stable austenitic texture, prevent the formation of a harmful precipitate deteriorating mechanical properties, such as σ phase, etc. and improve the lead oxide corrosion resistance and composite lead oxide corrosion resistance, therefore the lower limit of Ni was taken as 35.0%. If Ni is more than 65%, the effect enhancement is little even it is contained and the alloy becomes expensive, therefore the upper limit of Ni was taken as 65.0%.

Cr is essential to the enhancement of composite lead oxide corrosion resistance, if Cr is less than 20.0%, the enhancement is insufficient, therefore the lower limit of Ni was taken as

20.0%. If Cr is more than 35.0%, the effect enhancement is little even it is contained, and a harmful precipitate deteriorating mechanical properties, such as σ phase, etc. easily occurs, therefore the upper limit of Ni was taken as 35.0%.

Like Ti and Al, N is an element for enhancing the high-temperature strength. As is known from effects of N, Ti, Al on the composite lead oxide corrosion resistance shown in Fig. 2, Ti, Al markedly deteriorates the corrosion resistance, by contrast, N has almost no deterioration effect and is an optimum element for enhancing the high-temperature strength. 0.10% C must be contained to display the above property, thus the lower limit of N was taken as 0.10%. If C is more than 0.60%, it impairs the thermal workability, therefore the upper limit of Ni was taken as 0.60%.

Besides the above C, Si, Mn, Ni, Cr, N, if Mo 0.05 - 2.00%, W 0.05 - 2.00%, V 0.05 - 3.00%, Nb 0.05 - 3.00%, B 0.0005 - 0.0100% are added separately or by combining two or more of them, the high-temperature strength can be further raised without much deteriorating the high-temperature corrosion resistance. In this case, if each element is lower than its lower limit, the effects are small; if each element is more than its upper limit, the high-temperature corrosion resistance or the thermal workability is deteriorated.

If Al 0.01 - 0.50%, rear-earth elements 0.005 - 0.100%, Ca 0.0005 - 0.0200%, Mg 0.0005 - 0.0200% are added separately or by combining two or more of them, the thermal workability and the high-temperature toughness of each alloy can be further raised. In this case, if each element is lower than its lower limit, the effects are small; if each element is more than its upper limit, a harmful phase produces, and the thermal workability and the high-temperature toughness are deteriorated instead.

Next, the characteristics of invented alloy are clarified by actual examples as compared with comparison alloys.

Table 1 show chemical compositions of invented alloys, con-

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ventional alloys and comparison alloys. In Table 1, A, B are conventional alloys, A is 21-4N steel and B is an N-based alloy, C and D are comparison alloys, E and F are first invented alloys, G is a second first invented alloy, H is a third invented alloy, and J is a fourth alloy.

Table 2 shows corrosion losses in case that the alloy A - J of Table 1 are forged, afterward heated at 1,050°C x 1/2 hr to make a solid solution and then cooled, subsequently time-effect treated at 800°C x 4 hr and then immersed for 1 hr with lead oxide of 960°C or a molten composite lead oxide of 900°C for measuring the high-temperature corrosion resistance, and the

high-temperature tensile strength was measured with a test piece of a parallel part of 10ϕ x 50 mm applied with said treatments.

Table 1

	Chemical Composition (wt%)													
	C	Si	Mn	Ni	Cr	N	Mo	W	Nb	B	Al	Ti	Ca	Rare-Earth Element
A	0.55	0.08	9.16	4.4	21.4	0.48								
B	0.08	0.28	0.21	73.2	15.6				0.93		0.85	2.65		
C	0.11	0.28	8.10	48.2	28.8						1.81	2.70		
D	0.14	0.22	3.80	48.4	28.5	0.86								
E	0.13	0.25	5.85	48.3	28.3	0.86								
F	0.14	0.28	7.98	48.6	28.6	0.49								
G	0.14	0.24	8.25	48.5	29.0	0.38	0.44		0.55					
H	0.08	0.26	8.10	47.6	28.5	0.37					0.021		0.0083	0.030
J	0.13	0.25	7.76	48.3	28.0	0.34		0.85		0.0025			0.0064	0.027

Table 2

	High-Temp. Corrosion Resistance		Hardness at Room Temp. (HRC)	High-Temp. Tensile Strength 900°C· (kg/mm²)
	Lead oxide corrosion loss 900°Cx1hr (g/dm²·hr)	Composite Lead oxide corrosion loss 900°C (g/dm²·hr)		
A	26.5	2.1	32	19
B	2.5	85.3	32	25
C	24.0	66.5	33	26
D	2.1	85.0	30	24
E	2.5	1.9	30	24
F	2.3	1.9	31	24
G	3.5	2.1	32	26
H	2.5	2.0	30	24
J	2.8	2.2	31	26

For mechanical properties of alloys A - J applied with said heat treatment in accordance with use conditions of said exhaust valve for gasoline engine, as is evident from Table 2, all the alloys A - J can give desirable hardness HRC 30 -88. The high-

temperature strength becomes a value as low as 19 kg/cm^2 from conventional alloy A being a Fe-based alloy, other alloys C - J show values equal to alloy B being an Ni-based alloy (24 - 26 kg/cm^2) because they contain a necessary amounts of Ni and N, Al, Ti as reinforcement elements, particularly, the high-temperature strength of alloys G, J becomes the maximum by containing Mo, Nb, W, B, etc. as elements further enhancing the strength. For the high-temperature corrosion resistance, the alloy A has excellent corrosion loss of S-containing composite lead oxide (2.1 $g/dm^2 \cdot hr$) because it is a Fe-based alloy but poor lead oxide corrosion loss (26.5 $g/dm^2 \cdot hr$) because it has a low Ni content. The alloy A is a Fe-based alloy, by contrast, the alloy B is an Ni-based alloy and therefore shows a totally contrast tendency, it has an excellent lead oxide corrosion loss (25 $g/dm^2 \cdot hr$) but a very poor composite lead oxide corrosion loss (85.3 $g/dm^2 \cdot hr$). The alloy C contains a necessary amount of Mn but considerable amounts of Al, Ti, therefore both the lead oxide corrosion loss and composite lead oxide corrosion loss are large (24.0 $g/dm^2 \cdot hr$, 66.5 $g/dm \cdot hr$). The alloy D contains necessary amounts of Ni and N but an amount of Mn as low as 3.8%, therefore it has excellent lead oxide corrosion loss (2.1 $g/dm^2 \cdot hr$) but very poor composite lead oxide corrosion loss (85.0 $g/dm^2 \cdot hr$). By contrast, the alloy E - J being the invented alloys have excellent corrosion

resistance equal to the N-based alloy (lead oxide corrosion loss 2.1 - 3.5 g/dm·hr) and much more excellent high-temperature corrosion resistance than the N-based alloy (composite lead oxide corrosion loss 1.9 - 2.2 $g/dm^2 \cdot hr$). From this, it is known that the invented alloys not only have excellent high-temperature strength and lead oxide corrosion resistance but also have excellent corrosion resistance of composite lead oxide containing S and other impurities, thus they have very excellent corrosion resistance to the high-temperature combustion gas.

Next, Fig. 3 shows the thermal workability of invented alloys, in Fig. 3, E, G, H, J are the first invented alloy to the fourth invented alloy having same compositions as alloys shown in said Table 1 and Table 2. In a high-temperature torsion test, samples were cut out from the surface layer part of a 50 kg ingot in a direction perpendicular to columnar crystal, and test pieces of 10ϕ x 30 mm in parallel part were used. The test pieces were kept at a revolution of 25 rpm, heating temperatures of 900°C, 1,000°C, 1,100°C, 1,200°C as test conditions for 15 min and then measured.

As is evident from the test results in Fig. 3, the alloy H containing 0.0083% of Ca and 0.080% of rare-earth elements being the third and fourth invented alloys and the alloy J containing 0.0064% of Ca and 0.0027% of rare-earth elements being the third

and fourth invented alloys show a higher number of rupture twist than the alloys E, G being the first and second invented alloys. From this, it is known that the third and fourth invented alloys containing Ca, rare-earth elements are excellent in the thermal workability.

As described above, the invented alloys have excellent high-

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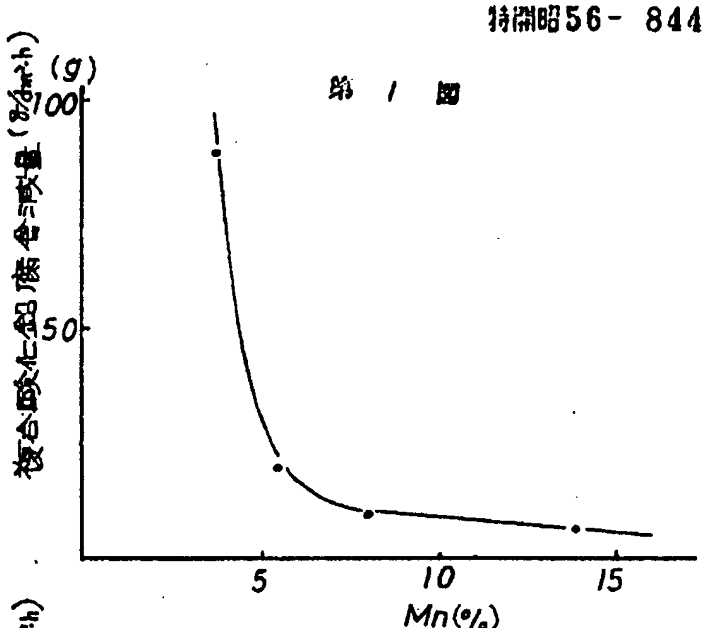
temperature strength equal or higher than the Ni-based alloy and more excellent corrosion resistance against a high-temperature combustion gas than the Ni-based alloy by containing C 0.05 - 0.25%, Si 1.00% or less, Mn 5.0 - 15.0%, Ni 35.0 - 65.0%, Cr 20.0 - 35.0%, N 0.10 - 0.60% and, as needed, Mo 0.05 - 2.00%, W 0.05 - 2.00%, V 0.05 - 3.00%, Nb 0.05 - 3.00%, B 0.0005 - 0.0100%, further enhance the thermal workability and the high-temperature toughness by containing Al 0.01 - 0.50%, rear-earth elements 0.005 - 0.100%, Ca 0.0005 - 0.0200%, Mg 0.0005 - 0.0200%, and the invented alloys are producible with the dissolution of air and are heat-resistant alloys having excellent high-temperature corrosion resistance and producible much cheaply than the bush metal of stellite, thus this invention makes a great contribution to the industry.

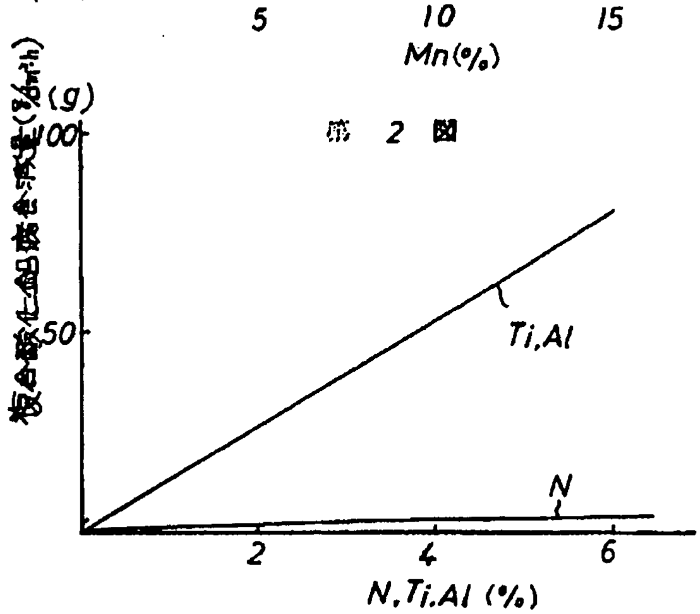
IV. Brief Description of the Drawings

Fig. 1 is diagram showing effect of Mn on composite lead oxide corrosion resistance, Fig. 2 is diagram showing effect of N, Ti, Al on composite lead oxide corrosion resistance, and Fig. 3 shows number of rupture twist of invented alloys at the heating temperatures.

第 1 図



第 2 図



KEYS:

Fig. 1

Composite lead oxide corrosion loss ($g/dm^2 \cdot hr$)

Mn (%)

Fig. 2

Composite lead oxide corrosion loss ($g/dm^2 \cdot hr$)

N, Ti, Al (%)

第 3 図

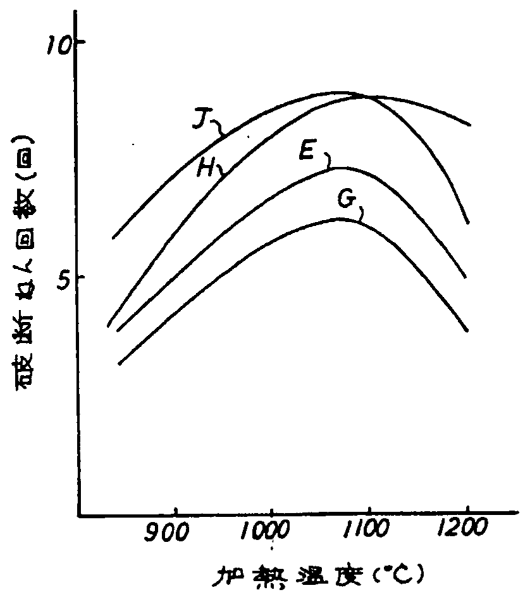


Fig. 3

Number of rupture twist

Heating temperature (°C)

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☐ 1. Document ID: JP 56084445 A

L1: Entry 1 of 2 File: JPAB Jul 9, 1981

PUB-NO: JP356084445A
DOCUMENT-IDENTIFIER: JP 56084445 A
TITLE: HEAT-RESISTANT ALLOY HAVING EXCELLENT CORROSION RESISTANCE AT HIGH TEMPERATURE

PUBN-DATE: July 9, 1981

INVENTOR-INFORMATION:

NAME	COUNTRY
KATO, SATOSHI	

ASSIGNEE-INFORMATION:

NAME	COUNTRY
AICHI STEEL WORKS LTD	

APPL-NO: JP54160670
APPL-DATE: December 10, 1979

US-CL-CURRENT: 420/453
INT-CL (IPC): C22C 38/18; C22C 19/05; C22C 30/00; C22C 38/18

ABSTRACT:

PURPOSE: To obtain an inexpensive heat-resistant alloy which is excellent in corrosion resistance and strength at high temperatures by a method in which part of Ni of an Ni-based alloy is replaced with Mn and appropriate amounts of elements capable of raising strength at high temperature and C and N producible with the dissolution of the air are added to the Ni-based alloy.

CONSTITUTION: A heat-resistant alloy contains 0.05∼0.25wt% C, 1.00wt% or less Si, 5.0∼15.0wt% Mn, 35.0∼65.0wt% Ni, 20.0∼35.0wt% Cr, 0.10∼0.60wt% N, and Fe and impurity elements, together, as needed, with one or more of 0.05∼ 2.00wt% Mo, 0.05∼2.00wt% W, 0.05∼3.00wt% V, 0.05∼3.00wt% Nb, and 0.0005∼0.0100wt% B and also one or more of 0.01∼0.5wt% Al, 0.005∼0.100wt% rare earth elements, 0.0005∼0.020wt% Ca, and 0.0005∼0.0200wt% Mg. The heat- resistant alloy excellent in composite lead oxide corrosion resistance against S- compounds can be obtained, and is suitable for the manufacture of the exhaust valve, etc., of gasoline engine.

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image

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☐ 2. Document ID: JP 56084445 A JP 88046141 B

L1: Entry 2 of 2 File: DWPI Jul 9, 1981

DERWENT-ACC-NO: 1981-61538D
DERWENT-WEEK: 198134

TITLE: Iron alloy contg. nickel, chromium and manganese - has resistance to high temp. corrosion, used in exhaust valves of petrol engines

PATENT-ASSIGNEE:

ASSIGNEE	CODE
AICHI SEIKO KK	AICI

PRIORITY-DATA: 1979JP-0160670 (December 10, 1979)

PATENT-FAMILY:

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APPLICATION-DATA:

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JP 56084445A	December 10, 1979	1979JP-0160670	

INT-CL (IPC): C22C 19/05; C22C 30/00; C22C 38/18

ABSTRACTED-PUB-NO: JP 56084445A
BASIC-ABSTRACT:

Alloy consists of C 0.05-0.25%, Si 1.00 or less, Mn 5.0-15.0%, Ni 35.0-65.0%, Cr 20.0-35.0%, N 0.10-0.60% and unavoidable impurities. The alloy may contain one or more of Mo 0.05-2.00%, W 0.05-2.00%, V 0.05-3.00%, Nb 0.05-3.00% and B 0.0005-0.0100%, and also one or more of Al 0.01-0.50%, rare earth elements 0.005-0.100%, Ca 0.0005-0.2000% and Mg 0.0005-0.0200%.

Mn additive improves resistance to corrosion caused by Pb oxide melt contg. sulphur. The alloy is easily melted in air, because the alloy does not contain such elements as Ti, Al, etc. which reduce high temp. corrosion resistance though improve high temp. strength.

TITLE-TERMS: IRON ALLOY CONTAIN NICKEL CHROMIUM MANGANESE RESISTANCE HIGH TEMPERATURE CORROSION EXHAUST VALVE GASOLINE ENGINE

DERWENT-CLASS: M27

CPI-CODES: M26-B08; M26-B08C; M26-B08J; M26-B08M; M27-A04; M27-A04C; M27-A04M; M27-A04N;

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image

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㊸公開　昭和56年(1981) 7月9日

発明の数　4
審査請求　未請求

（全 5 頁）

㊺高温耐食性の優れた耐熱合金

㉑特　　願　昭54—160670
㉒出　　願　昭54(1979)12月10日

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明　　細　　書

1．発明の名称　高温耐食性の優れた耐熱合金

2．特許請求の範囲

(1) 重量比にしてC 0.05〜0.25%，Si 1.00%以下，Mn 5.0〜15.0%，Ni 35.0〜65.0%，Cr 20.0〜35.0%，N 0.10〜0.60%を含有して残部Feならびに不純物元素からなることを特徴とする高温耐食性の優れた耐熱合金。

(2) 重量比にしてC 0.05〜0.25%，Si 1.00%以下，Mn 5.0〜15.0%，Ni 35.0〜65.0%，Cr 20.0〜35.0%，N 0.10〜0.60%を含有し、さらにMo 0.05〜2.00%，W 0.05〜2.00%，V 0.05〜3.00%，Nb 0.05〜3.00%，B 0.0005〜0.0100%のうち1種ないし2種以上を含有し残部Feならびに不純物元素からなることを特徴とする高温耐食性の優れた耐熱合金。

(3) 重量比にしてC 0.05〜0.25%，Si 1.00%以下，Mn 5.0〜15.0%，Ni 35.0〜65.0%，Cr 20.0〜35.0%，N 0.10〜0.60%を含有し、さらにAl 0.01〜0.50%，希土類元素0.005〜0.100%，Ca 0.0005〜0.0200%，Mg 0.0005〜0.0200%のうち1種ないし2種以上を含有して残部Feならびに不純物元素からなることを特徴とする高温耐食性の優れた耐熱合金。

(4) 重量比にしてC 0.05〜0.25%，Si 1.00%以下，Mn 5.0〜15.0%，Ni 35.0〜65.0%，Cr 20.0〜35.0%，N 0.10〜0.60%を含有し、さらにMo 0.05〜2.00%，W 0.05〜2.00%，V 0.05〜3.00%，Nb 0.05〜3.00%，B 0.0005〜0.0100%のうち1種ないし2種以上とAl 0.01〜0.50%，希土類元素0.005〜0.100%，Ca 0.0005〜0.0200%，Mg 0.0005〜0.0200%のうち1種ないし2種以上を含有し残部Feならびに不純物元素からなることを特徴とする高温耐食性の優れた耐熱合金。

3．発明の詳細な説明

本発明はガソリン機関用排気弁等耐熱材料に用いられる高温耐食性、高温強度に優れ、かつ大気溶解で製造が可能な高温耐食性合金に関するもの

である。

ガソリン機関の排気弁は高温腐食性の排気ガスにさらされ、しかも800℃以上の高温下で高速運動するなど苛酷な条件で使用される。高温の燃焼ガス中にはCO_2、H_2Oおよび残留O_2等が存在し、これらによって酸化作用を受け、特にアンチノック剤としてガソリン中に添加されている四エチル鉛又は四メチル鉛が燃焼して生成した酸化鉛、さらにはガソリン中に不純物として含まれるS、Cl、Br、P等との反応生成物($PbSO_4$、PbBrCl、$Pb_3(PO_4)_2$等)によって弁フエース部が激しく侵食される。

また、弁ばねの張力および弁自身の慣性力により着座時に弁首部に大きな引張応力および曲げ応力が作用する。

現在、欧米および日本においてガソリン機関の排気弁用材料として最も多用されているものに21-4N鋼(Fe-21Cr-9Mn-4Ni-0.5C-0.4N)がある。

しかし、最近の高性能機関においてはさらに高出力あるいは高速化しつつあり、このような苛酷な条件下では前記の21-4N鋼では高温耐食性や高温強度が不足し、使用に耐え難い状況も出現し、21-4N鋼より数段優れた高温耐食性および高温強度を有する合金の開発が要望されている。

このような情勢に対応して、近時排気弁にNi基合金を使用したり、ステライト合金の盛金弁を使用する傾向にある。しかしながらNi基合金は材料が高価なため弁コストが高くなり、その上高負荷機関ではSを含む高温燃焼ガスに対する耐食性が不十分である。

また、ステライト合金の盛金弁は盛金作業が煩雑であり、多くの人手を要するため弁コストが高くなり、しかも高負荷機関では排気弁としての諸性能も不十分である。

本発明はかかる従来鋼の欠点を解消するもので、発明者が種々研究を重ねた結果、Ni基合金のNiの一部をMnで置換し、Mnを含有させたことによりS化合物を含む溶融酸化鉛による耐食性(以下複合酸化鉛耐食性という)を改善し、さらに高温での強度を向上させる強化元素として、Ti、Al等のように高温での耐食性を害する作用がなく、しかも大気溶解で製造が可能なN、Cを使用することによって、従来使用されているNi基合金に比べ優れた高温耐食性を有するとともに同等の高温強度を有するものであり、かつ格段に安価な高温耐食性合金である。

また、本発明合金は弁製造に際してステライト盛金のような複雑な工程を必要とせず、従来の21-4N鋼排気弁と同様にアップセット鍛造により製造可能であるためステライト合金の盛金弁と比べてもより安価で、かつ優れた性能を有するものである。

以上のように本発明合金は高温耐食性、高温耐酸化性および高温強度において優れたもので、排気弁のほか各種耐熱部品、耐熱工具用材、高温摺動部材などに広く使用できるものである。

以下に本発明合金について詳述する。

第1発明合金は、重量比にしてC0.05~0.25%，Si1.00%以下、Mn5.0~15.0%，Ni35.0~65.0%，Cr20.0~35.0%，N0.10~0.60%を含有したもので、第2発明合金は第1発明合金にMo0.05~2.00%，W0.05~2.00%，V0.05~3.00%，Nb0.05~3.00%，B0.0005~0.0100%のうち1種ないし2種以上を含有し第1発明合金の高温耐食性をあまり劣化させることなく高温強度を一層高めたもので、第3発明合金は第1発明合金にAl0.01~0.50%，希土類元素0.005~0.100%，Ca0.0005~0.0200%，Mg0.0005~0.0200%のうち1種ないし2種以上を含有し第1発明合金の熱間加工性、高温靱性を一層高めたもので、第4発明合金は第2発明合金にAl0.01~0.50%、希土類元素0.005~0.100%，Ca0.0005~0.0200%，Mg0.0005~0.0200%のうち1種ないし2種以上を含有させ第2発明合金の熱間加工性、高温靱性を一層高めたものである。

以下に本発明合金の成分限定理由について説明する。

Cは一部地質に固溶してそれを強化するとともに炭化物を形成し素地を強化する。炭化物による素

地強化は効果的ではあるが0.05%未満では少なく、0.25%を越えると熱間加工性を著しく害するのでその範囲を0.05~0.25%とした。

Siは地質に固溶してそれを強化し、また高温耐酸化性を改善するが、1.00%を越えると高温酸化鉛耐食性を害するので上限を1.00%とした。

Mnは高Ni合金のS化合物およびその他の不純物を含む複合酸化鉛耐食性を著しく改善する。第1図は複合酸化鉛耐食性におよぼすMnの影響を示したものであり、これからしてMnが5.0%以上で著しく耐食性を改善することが知られる。このためMnの下限を5.0%とした。

また、Mnが15.0%を越えると低融点のNi-Mn共晶が生成し、熱間加工性が著しく困難となるため上限を15.0%とした。

Niは安定なオーステナイト組織を得、シグマ相等の機械的性質を劣化させる有害な析出物の生成を防止し、酸化鉛ならびに複合酸化鉛耐食性を向上させるために不可欠であり、したがって、Niの下限を35.0%とした。また、65.0%を越えて含有させても効果の向上が小さく高価となるので上限を65.0%とした。

Crは複合酸化鉛耐食性の向上に不可欠であり、20.0%未満では不十分であるので下限を20.0%とした。また35.0%を越えて含有させても効果の向上が小さく、シグマ相等の機械的性質を劣化させる有害な析出物がでやすくなるので上限を35.0%とした。

NはTi、Alと同様に高温強度を向上させる元素である。第2図に示した複合酸化鉛耐食性におよぼすN、Ti、Alの影響から知られるようにTi、Alが著しく耐食性を劣化させるのに対して、Nは劣化作用が殆んどなく、高温強度を向上させるには最適な元素である。上記の性能を発揮させるには0.10%以上含有させる必要があり下限を0.10%とした。また0.60%を越えて含有させると熱間加工性を害するので上限を0.60%とした。

以上のC、Si、Mn、Ni、Cr、Nの他に0.05~2.00%のMo、0.05~2.00%のW、0.05~3.00%のV、0.05~3.00%のNb、0.0005~0.0100%のBを単独あるいは2種以上を複合して添加すれば高温耐食性をあまり劣化させることなく高温強度を一層高めることができる。この場合各元素とも下限未満では効果が小さく、上限を越えて添加した場合には高温耐食性あるいは熱間加工性を劣化させる。

さらに、以上の各成分の合金に対して0.01~0.50%のAl、0.005~0.100%の希土類元素、0.0005~0.0200%のCa、0.0005~0.0200%のMgを単独あるいは2種以上複合して添加すれば各合金の熱間加工性、高温靱性を一層向上させることができる。この場合各元素とも下限未満では効果が小さく、上限を越えて添加した場合には有害相が生成し、熱間加工性、高温靱性をかえって劣化させる。

つぎに本発明合金の特徴を従来合金、比較合金と比べ実施例でもって明らかにする。

第1表は本発明合金、従来合金、比較合金の化学成分を示すものである。

第1表

	化学成分(重量%)													
	C	Si	Mn	Ni	Cr	N	Mo	W	Nb	B	Al	Ti	Ca	希土類元素
A	0.55	0.08	9.16	4.4	21.4	0.43								
B	0.09	0.28	0.21	73.2	15.6				0.98		0.85	2.65		
C	0.11	0.28	8.10	48.2	28.8						1.81	2.70		
D	0.14	0.22	3.80	48.4	28.5	0.36								
E	0.18	0.25	5.85	48.3	28.3	0.36								
F	0.14	0.23	7.98	48.6	28.6	0.49								
G	0.14	0.24	8.25	48.5	29.0	0.38	0.44		0.55					
H	0.08	0.26	8.10	47.6	28.5	0.37					0.021		0.0083	0.030
J	0.13	0.25	7.76	48.3	28.0	0.34		0.85		0.0025			0.0064	0.027

第1表においてA、Bは従来合金で、Aは21−4N鋼、BはNi基合金で、C、Dは比較合金で、E、Fは第1発明合金、Gは第2発明合金、Hは第3発明合金、Jは第4発明合金である。

第2表は第1表のA〜J合金を鍛造後、1050℃×1/2h固溶化加熱後水冷し、ついで800℃×4h時効処理し、高温耐食性については960℃の酸化鉛または900℃の溶融複合酸化鉛で1時間浸漬した場合の腐食減量を示し、高温引張り強さについては、前記処理を施した平行部10φ×50mmの試片を用いて測定した。

第2表

	高温耐食性		室温かたさ	高温引張強さ
	酸化鉛腐食減量 960℃×1h(g/dm²·h)	複合酸化鉛腐食減量 900℃×1h(g/dm²·h)	(HRC)	900℃·(kg/mm²)
A	26.5	2.1	32	19
B	2.5	35.3	32	25
C	24.0	66.5	33	26
D	2.1	35.0	30	24
E	2.5	1.9	30	24
F	2.8	1.9	31	24
G	3.5	2.1	32	26
H	2.5	2.0	30	24
J	2.8	2.2	31	26

ガソリン機関用排気弁の使用条件に合わせて前記熱処理を施したA〜J合金の機械的性質は第2表から明らかなよう、その硬さはA〜J合金のいずれもHRC30〜33と所望の硬さを得ることができた。高温強度については、従来合金であるA合金がFe基合金であることから19kg/mm²と低い値となっているが、その他のC〜J合金は必要量のNi量と強化元素としてN、Al、Tiを含有していることから24〜26kg/mm²とNi基合金であるB合金と同等の値を示し、なかでもG、J合金は高温強度をさらに向上させる元素としてMo、Nb、W、B等を含有させたことにより最も高くなっている。また、高温耐食性については、A合金がFe基合金であることからS化合物を含む複合酸化鉛腐食性については2.1g/dm²·hと優れているが、酸化鉛腐食減量はNi含有量が低いことから26.5g/dm²·hと劣っている。B合金はA合金がFe基合金であるのに対してNi基合金であることから全く反対の傾向を示しており、酸化鉛腐食減量が2.5g/dm²·hと優れているが、複合酸化鉛腐食減量については35.3g/dm²·hと大変劣っている。C合金についてはMn量が必要量含有されてはいるが、多量のAl、Tiを含有していることから酸化鉛および複合酸化鉛腐食減量がともに大きく24.0g/dm²·h、66.5g/dm²·hとともに劣っている。D合金についてはNi量およびN量については必要量含有されているがMn量が3.30%と低いことから酸化鉛腐食減量は2.1g/dm²·hと優れているが複合酸化鉛腐食減量は35.0g/dm²·hと大変劣っている。これらに対して本発明合金であるE〜J合金は必要量のNi、Mn等を含有させたことにより酸化鉛腐食減量については2.1〜3.5g/dm²·hとNi基合金と同等の優れた耐食性を有し、さらに複合酸化鉛耐食性についてはその腐食減量が1.9〜2.2g/dm²·hとNi基合金に比べ格段に優れた高温耐食性を示している。これからしても本発明合金が高温強度および酸化鉛腐食性のみならずS化合物および他の不純物を含む複合酸化鉛腐食性にも優れ高温燃焼ガスに対する耐食性が非常に優れていることがわかる。

つぎに第3図は本発明合金の熱間加工性について示したもので、図中E、G、H、Jは前記第1および第2表に示した合金と同一組成からなる第1発明合金ないし第4発明合金である。高温ねじり試験に際しては50kg鋼塊表層部から柱状晶に直角な方向に切出し、平行部10φ×30mmの試片を用いた。試験条件としては回転数25r.p.m、加熱温度900℃、1000℃、1100℃、1200℃の各温度で15分間保持した後、測定した。

試験結果は第3図から明らかなように、第3発明および第4発明合金である0.0033%のCaおよび0.030%の希土類元素を含有させたH合金、さらに0.0064%のCaおよび0.027%の希土類元素を含有させたJ合金は第1発明および第2発明合金であるE、G合金に比べ高い破断ねん回数を示している。これからしてもCa、希土類元素を含有させた第3発明および第4発明合金が熱間加工性についても優れていることがわかる。

上述の如く、本発明合金は35.0〜65.0%のNi、20.0〜35.0%のCr合金に、5.0〜15.0%

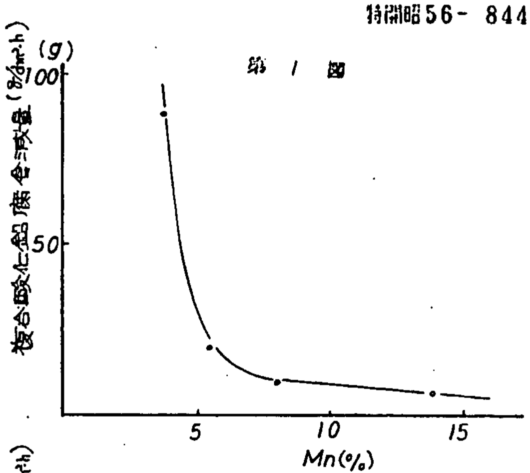
のMnと0.10～0.60%のNを含有させ、かつ必要に応じてMo、W、V、Nb、Bをさらに含有させたことにより、Ni基合金と同等もしくはそれ以上の高温強度を有するとともにNi基合金に比べて優れた高温燃焼ガス耐食性を有しており、さらにAl、希土類元素、Ca、Mgを含有させたことにより熱間加工性および高温靭性を一層向上させたものであり、かつ本発明合金は大気溶解で製造が可能なものでNi基合金およびステライト合金の感金に比べ格段に安価に製造が可能な高温耐食性の優れた耐熱合金で産業上寄与するところ極めて大である。

4．図面の簡単な説明

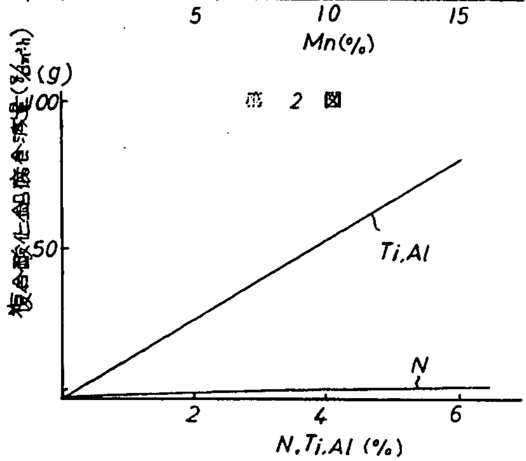
第1図は複合酸化鉛耐食性におよぼすMnの影響を示した線図、第2図は複合酸化鉛耐食性におよぼすN、Ti、Alの影響を示した線図、第3図は本発明合金の各加熱温度における破断ねん回数を示したものである。

特許出願人
愛知製鋼株式会社

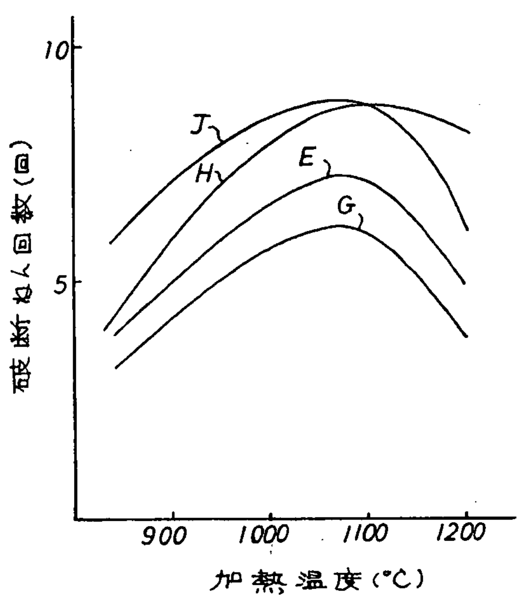
第1図



第2図



第3図



HEAT-RESISTANT ALLOY HAVING EXCELLENT CORROSIONRESISTANCE AT HIGH TEMPERATURE

Patent Number: JP56084445
Publication date: 1981-07-09
Inventor(s): KATO SATOSHI
Applicant(s): AICHI STEEL WORKS LTD
Requested Patent: JP56084445
Application Number: JP19790160670 19791210
Priority Number(s):
IPC Classification: C22C38/18; C22C19/05; C22C30/00; C22C38/18
EC Classification:
Equivalents: JP1506501C, JP63046141B

Abstract

PURPOSE:To obtain an inexpensive heat-resistant alloy which is excellent in corrosion resistance and strength at high temperatures by a method in which part of Ni of an Ni-based alloy is replaced with Mn and appropriate amounts of elements capable of raising strength at high temperature and C and N producible with the dissolution of the air are added to the Ni-based alloy.
CONSTITUTION:A heat-resistant alloy contains 0.05-0.25wt% C, 1.00wt% or less Si, 5.0-15.0wt% Mn, 35.0-65.0wt% Ni, 20.0-35.0wt% Cr, 0.10-0.60wt% N, and Fe and impurity elements, together, as needed, with one or more of 0.05- 2.00wt% Mo, 0.05-2.00wt% W, 0.05-3.00wt% V, 0.05-3.00wt% Nb, and 0.0005-0.0100wt% B and also one or more of 0.01-0.5wt% Al, 0.005-0.100wt% rare earth elements, 0.0005-0.020wt% Ca, and 0.0005-0.0200wt% Mg. The heat- resistant alloy excellent in composite lead oxide corrosion resistance against S- compounds can be obtained, and is suitable for the manufacture of the exhaust valve, etc., of gasoline engine.

CLIPPEDIMAGE= JP356084445A

PAT-NO: JP356084445A

DOCUMENT-IDENTIFIER: JP 56084445 A

TITLE: HEAT-RESISTANT ALLOY HAVING EXCELLENT CORROSION RESISTANCE AT HIGH TEMPERATURE

PUBN-DATE: July 9, 1981

INVENTOR-INFORMATION:
NAME
KATO, SATOSHI

ASSIGNEE-INFORMATION:

NAME	COUNTRY
AICHI STEEL WORKS LTD	N/A

APPL-NO: JP54160670

APPL-DATE: December 10, 1979

INT-CL (IPC): C22C038/18;C22C019/05 ;C22C030/00 ;C22C038/18

US-CL-CURRENT: 420/453

ABSTRACT:

PURPOSE: To obtain an inexpensive heat-resistant alloy which is excellent in corrosion resistance and strength at high temperatures by a method in which part of Ni of an Ni-based alloy is replaced with Mn and appropriate amounts of elements capable of raising strength at high temperature and C and N producible with the dissolution of the air are added to the Ni-based alloy.

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0.05∼3.00wt% Nb, and 0.0005∼0.0100wt% B and also one or more of 0.01∼0.5wt% Al, 0.005∼0.100wt% rare earth elements, 0.0005∼0.020wt% Ca, and 0.0005∼0.0200wt% Mg. The heat- resistant alloy excellent in composite lead oxide corrosion resistance against S- compounds can be obtained, and is suitable for the manufacture of the exhaust valve, etc., of gasoline engine.